REDUCING VOLATILE ORGANIC COMPOUNDS DURING THE MATURITY STAGE OF DIFFERENT COMPOSTED ORGANIC WASTES BY USING SOME CLAY MINERALS AS A NATURAL REMEDIATION

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ABSTRACT:

A trail was carried out on reducing the volatile organic compounds (VOCs) during the maturity stage of different composted organic wastes (*i.e.*, town refuse, sugarcane factories, animal residues and plant residues) by using three kinds of clay minerals (*i.e.*, montmorillonite, kaolinite and attapulgite) as a natural remediation. The total released volatile organic compounds as air organic pollutants from each of the tested composted organic wastes were determined by using the GC-mass method. The released VOCs are namely ethanol, acetic acid, acetone, n-propanol, cyclohexane, n-heptane, octane, benzene, chlorobenzene, ethylbenzene, toluene, dichloromethane, xylene, methyl chloride and trichloroethane.

The obtained data showed that the released VOCs recorded the greatest values in case of the composted sugarcane wastes, while the lowest ones were associated with the composted town refuse wastes. On the other hand, the composted animal and plant residues exhibited values of released air volatile organic pollutants represent an intermediate case between the other composted organic substances. Thus, it could be arranged the different studied composted organic wastes according to the released amounts of VOCs values in an ascending order of composted sugarcane wastes > composted plant residues > composted animal residues > composted town refuse wastes.

Accordingly, composted sugarcane wastes that showed the greatest released VOCs values were chosen for a natural remediation by using the tested clay minerals (*i.e.*, montmorillonite, kaolinite and Attapulgite) at applied two rates of 5 and 10 % and during two interval periods of 24 and 48 hours. The obtained results showed that the percentages of released VOCs as a result of treating composted sugarcane wastes with the clay minerals of montmorillonite, kaolinite, and attapulgite at the rates of 5 & 10 % reached 91.20 & 87.50, 78.76 & 60.42 and 52.46 & 35.42 % of the released amounts from the untreated ones at the fixed time of 24 h vs the corresponding values of 9.49 & 8.38, 6.25 & 6.04 and 5.89 & 4.06 % at an interval period of 48 h, respectively. So, it could be categorized the tested clay minerals as a natural remediation according to their immobilization for the released VOCs into an ascending order: attapulgite > kaolinite > montmorillonite.

Key words: Composted organic wastes, volatile organic compounds, remediation of released air pollutants by using clay minerals.

INTRODUCTION:

Volatile organic compounds (VOCs) are a large group of anthropogenic (xenobiotic) or biogenic compounds with relatively high vapor pressures. VOCs are also characterized by their low water solubility. VOCs in gaseous streams are potential air pollutants due to their malodrous and hazardous properties. Eye and throat irritation, damage to liver, central nervous system,

all may occur due to the prolonged exposure to VOCs. VOCs may also carcinogenic effects (**Das** *et al.*, **2004**). In addition; VOCs can contribute to global warming, stratospheric ozone depletion and tropospheric ozone formation (**Komilis** *et al.*, **2004**). For this reason VOCs are being subject to increasingly severe constrains.

At present, solid waste management, particularly the organic fraction is becoming a global problem in developed countries (**Pagans** *et al.*, 2007). Composting is a technology widely used for recycling organic wastes. Composting exhaust gases are characterized by high flow rates and pollutant concentrations. VOCs are among the major pollutants but there have been few studies on VOCs from composting facilities (**Tolvanen** *et al.*, 1998; **Turan** *et al.*, 2007).

To avoid atmospheric contamination, exhaust gases from composting should be treated before release to the atmosphere (**Pagans** *et al.*, **2007**). A number of physicochemical processes including adsorption, incineration and absorption can be used to treat VOCs, but the costs for chemicals and fuels as well as further treatment or disposal of secondary wastes are increasingly inhibiting adoption of these solutions (**Torkian** *et al.*, **2003**). Application of different additives to compost is one of the ways for reducing of the excessive amounts of VOCs.

The risk of compost pollution by organic pollutants remains even if separately collected organic waste is composted, because of aerial deposition or accidental (e.g., via the increasingly ubiquitous plastic debris (**Thompson** *et al.*, **2004**) and deliberate input of pesticide application such as chemicals to organic materials. Consequently, the input of PAHs, PXBs, and PCDD/Fs to the soil via compost application may be equal to or even higher than that introduced by aerial deposition or the application of other organic fertilizers such as sewage sludge or manure (Herter *et al.*, **2003**). To assure a sustainable soil quality, the input of organic pollutants to the soil has to be minimized. Conversely, the risk of soil pollution due to compost application has to be balanced with the soil-improving qualities of the compost, such as the stability of the soil particles, its pore volume, water capacity, organic matter content, and the related carbon and nitrogen content (**Timmermann** *et al.*, **2003**).

Generally, based on the researches conducted to date, it would appear that the sorption of organic pollutants by the natural materials is not the result of one mechanism but of several mechanisms. The mechanisms involved in the reducing of organic pollutants from compost with natural material, as mentioned by many researchers (Schneegurt *et al.*, 2001 and Brown *et al.*, 2000).

The objectives of this work were carried out to evaluate the reducing efficiency of released volatile organic compounds (VOCs) emitted from some composted organic wastes by using the different kinds of clay minerals as a natural remediation, *i.e.*, montmorillonite, kaolinite and attapulgite minerals.

MATERIALS and METHODS:

Materials:

Four sources of the composted organic wastes were chosen, *i.e.*, town refuse, the sugarcane factories, animal residues and plant residues to determine the volatile organic compounds (VOCs, air pollutants). After that, a remediation process was carried out for the organic compost which exhibited the greatest amount of the released VOCs by using some clay minerals as a

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natural remediation, *i.e.*, montmorillonite, kaolinite and Attapulgite. The tested clay minerals were mixed with the chosen composted organic wastes at two rates of 5 and 10 % (w/w). The contents of released volatile organic compounds or pollutants were determined after two interval periods of 24 and 48hours.

Analytical methods:

The samples of studied composted organic wastes were dried and analyzed for pH, electrical conductivity (EC in dS/m) in aqueous extract which was obtained by mechanically shaking the organic samples with distilled water at a ratio of 1:10 w/v (solid:water) for 1 hour (**Chapman and Pratt, 1961**). Total N was measured in digested samples, N-forms (NH₄-N & NO₃-N) after extracted in 2N KCl (1:10 w/v) were determined using Kjeldahl methods (**Vandenabeele** *et al.*, **1990**). Total K was measured by using flamphotometry. Organic carbon content was determined by using Walkely and Black method (**Hesse, 1971**).

Measuring volatile organic compounds by using EPA method 8240C:

A portion of each organic compost sample was extracted at META by using a rapid LPLE method, as follows: Approximately 2 g of each sample was placed in a 30 mL Teflon® centrifuge tube with a Teflon® screw cap, and then 5.0 mL of methylene chloride containing surrogate compounds and about 2 g of anhydrous sodium sulfate were added to the sample. The soil/sodium sulfate was ground until free-flowing using a clean stainless steel spatula. Once ground, each sample was sealed and placed in a water bath at 80 °C for 5 minutes, followed by a vigorous 2 minute hand shake while still hot. Next, each sample was chilled in a cold water bath for about 2 minutes, and then centrifuged for about 2 minutes. A 1.0 mL aliquot of the solvent was removed with a syringe and split between META and CFAST for analysis.

The extracts were analyzed using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC) with a 5971A mass selective detector (MSD), a HP 7673 autosampler, and HP Chemstation software. The instrument was operated in the splitless mode with 1 μ L injections onto a 30 m x 0.25 mm x 0.25 μ m RTX-5 (5% phenylmethylsiloxane) capillary column. The run time to elute all the target compounds was about 35 minutes, but the full cycle time was about 60 minutes.

RESULTS AND DISCUSSION:

I. Main chemical characteristics of the tested composted organic wastes:

Solid organic wastes management is becoming one of the main agent problems which cause the dramatic changes in environmental chemical pollution in Egypt. Thus, composting of these wastes is representing an urgent technology for their recycling. During composting process, the exhaust gases are released by high flow rates, and such volatile organic pollutants (VOCs) are adversely affected the atmospheric zone.

To avoid atmospheric contamination, exhaust gases from composting should be treated before release to the atmosphere. A number of physicochemical processes including adsorption, incineration, and absorption can be used to treat VOCs. To assure a clean atmospheric zone, the input of organic pollutants to the atmosphere has to be minimized. Conversely, the risk of air pollution due to composting process of organic wastes has to be balanced with the application of different additives such as some clay minerals to compost as a natural remediation, which is one of the ways for reducing of

the excessive amounts of VOCs. In general, based on the researches conducted to date, it would appear that the sorption of organic pollutants by the natural materials is not the result of one mechanism but of several mechanisms, depending upon the nature and chemical composition of the treated composted organic wastes. The main chemical characteristics of the tested composted organic wastes are presented in Table (1).

Chemical characteristics	Composted town refuse wastes	Composted sugarcane wastes	Composted animal residues	Composted plant residues
pН	7.73	7.55	8.75	7.83
EC (dS m^{-1})	6.50	1.49	4.97	7.74
NH_4^+ (mg kg ⁻¹)	140.00	1078.00	182.00	210.00
$NO_3(mg kg^{-1})$	42.00	45.00	138	28.00
Total carbon %	16.10	19.45	14.21	29.02
Total nitrogen %	1.03	1.09	0.88	1.71
C/N ratio	15.63	17.84	16.15	16.97
Total potassium %	1.97	1.74	2.41	1.35

Table (1): Chemical characteristics of the tested composted organic wastes.

II. Released volatile organic pollutants from the different studied composted organic wastes during the maturity stage:

The volatile organic pollutant contents released from different organic composted organic wastes are presented in Table (2).

 Table (2): Organic volatile pollutant contents released from the different studied composted organic wastes.

Composted organic waste sources	Total amounts of volatile pollutant contents (mg kg- ¹)		
Composted town refuse wastes	1239		
Composted sugarcane wastes	2034		
Composted animal residues	1299		
Composted plant residues	1323		

The obtained data showed that composted sugarcane wastes recorded the greatest values of released volatile organic pollutants (VOCs) vs the lowest ones which were associated with the composted town refuse wastes. On the other hand, the released values of volatile organic pollutants from either animal or plant residues exhibited an intermediate range between the studied other organic substances. These results are in harmony with the maturity stages, however, the values of released volatile organic pollutants from the different studied composted organic wastes are proportionally adverse with the ratios of C/N, Table (1). Accordingly, the studied composted organic wastes could be arranged according to their power capacity for releasing VOCs into the following descending order: composted sugarcane wastes > composted plant residues > composted animal residues > composted town refuse wastes.

It is noteworthy to mention that C/N ratio of any composted organic substance is a function of its maturity stage. That scientific fact is in harmony with the obtained results, however, the relatively high C/N ratio (17.84) that associated with composted sugarcane wastes reflects immature stage as well as

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that is confirmed by the relatively high amount of the released volatile organic compounds (2034 mg kg⁻¹). The reverse was true for composted town refuse wastes whose characterized by an advanced stage of maturity, since such composted organic substance exhibited a relatively low C/N ratio (15.63) and fewer amounts of the released volatile organic compounds (1239 mg kg⁻¹).

So, the composted sugarcane wastes, which exhibited the greatest amounts of the released VOCs, were selected for a natural remediation process by using the tested clay minerals, *i.e.*, montmorillonite, kaolinite and Attapulgite. These clay minerals were mixed with the studied composted organic wastes at two rates of 5 and 10 % (w/w), and the contents of released volatile organic compounds or air pollutants were determined after two interval periods of 24 and 48 hours, besides the untreated composted ones (Control).

III. Effect of applying the tested clay minerals as a natural remediation process for the immobilization of released VOCs from composted sugarcane wastes:

One technology that has a considerable amount of attention is in situ immobilization of released VOCs fractions in the composted organic wastes by the addition of various amendments for increasing the proportion of the total VOCs burden within the solid phase by adsorption, incineration and absorption processes (Torkian et al., 2003). Data of the magnitude for various released VOCs fractions from composted sugarcane wastes as affected by the applied clay mineral rates are summarized in Table (3) and Figs. (1, 2 and 3). It is evident that the magnitude for various released VOCs fractions could be categorized into ethanol, acetic acid, acetone, n-propanol, cyclohexane, nchlorobenzene, ethylbenzene, heptane. octane. benzene, toluene, dichloromethane, xylene, methyl chloride, and trichloroethane). Generally, decreased in individual organic pollutant concentrations due to materials used at 5 and 10 %.

Whilst the application of the tested clay minerals had a greater effect on reducing various released VOCs fractions bioavailability at both the two applied rates and interval periods, with a significantly decreased for each of applied rate 10 % and time of 48 h as compared to a rate 5 % and time of 24 h. Also, the application of the studied three clay minerals to immobilize the released VOCs fractions in situ might provide an effective and sustainable solution for a natural remediation of contaminants in the tested organic compost. In general, the released VOCs contents showed a tendency to decrease by increasing the applied clay mineral rates and times, with a rather greater response for attapulgite, followed by kaolinite and montmorillonite. This may have been a result the pronounced differences for adsorption capacities of VOCs by the studied clay minerals, which are strongly dependent on their properties including cross-sectional area, polarizability, enthalpy of vaporization and critical volume by the multiple linear regression approach.

The percentages of released VOCs as a result of treating composted sugarcane wastes with the clay minerals of montmorillonite, kaolinite, and attapulgite at the rates of 5 & 10 % reached 91.20 & 87.50, 78.76 & 60.42 and 52.46 & 35.42 % of the released amounts from the untreated ones at the fixed time of 24 h vs corresponding values of 9.49 & 8.38, 6.25 & 6.04 and 5.89 & 4.06 % at an interval period of 48 h, respectively.

Table 3

24 h

48 h

Figure (1): Effect of the tested clay mineral of montmorillonite as a natural remediation at an applied rate of 10 % on reducing the released volatile organic compounds from composted sugar cane wastes after interval periods of 24h & 48 h.

24 h

48 h

Figure (2): Effect of the tested clay mineral of kaolinite as a natural remediation at an applied rate of 10 % on reducing the released volatile organic compounds from composted sugar cane wastes after interval periods of 24h & 48 h.

24 h

48 h

Figure (3): Effect of the tested clay mineral of attapulgite as a natural remediation at an applied rate of 10 % on reducing the released volatile organic compounds from composted sugar cane wastes after interval periods of 24h & 48 h.

So, it could be categorized the tested clay minerals as a natural remediation according to their immobilization for the released VOCs into an ascending order: attapulgite > kaolinite > montmorillonite. These results suggesting that the applied clay minerals have directly greater potential to immobilize the studied released VOCs in the studied contaminated sugarcane wastes, however, attapulgite potential was almost coupled with the noticeable residual effect of VOCs in the treated organic compost.

The aforementioned results can be interpreted on the base that reacts of applied clay minerals with the tested VOCs improved significantly with the progress of active adsorption and absorption sites. These findings are in harmony with those reported by Sheng and Boyd (1998) and Stevens et al. (1996) who reported that montmorillonite is bound primarily to the interlayer exchangeable cations and that the binding had only minor effects on the sorption of hydrophobic pollutants, such as the sorption of alkyl-substituted benzenes, on the siloxane surfaces. Qu et al. (2009) studied the adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCHs), and found that PCHs are capable of adsorbing volatile organic compounds (VOCs). The same authors reported that PCHs was synthesized by modifying bentonite with cetyltrimethylammonium bromide and dodecylamine. Adsorption of six volatile organic compounds including acetone, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene by PCHs was also investigated. It was observed that adsorption capacities of VOCs were strongly dependent on their properties including cross-sectional area, polarizability, enthalpy of vaporization and critical volume by the multiple linear regression approach. Furthermore, PCHs had higher adsorption affinity for the aliphatic hydrocarbon compound (acetone) than that for aromatic compounds, which could be attributed to the HOMO energy effects of VOCs. Therefore, PCHs could be attractive candidate adsorbents for the released VOCs.

Turan *et al.* (2009) studied the effective role of some natural materials for reducing the released VOCs during composting of poultry litter. They found that natural zeolite, expanded perlite, pumice and expanded vermiculite as natural materials were more effective for the reducing of VOCs. Also, their data are confirmed on the bases of VOCs generation was the greatest in the control treatment without any natural materials.

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خفض المركبات العضوية المتطايرة أثناء مرحلة النضج لمكمورات من المخلفات العضوية المختلفة باستخدام بعض معادن الطين كمعالجة طبيعية

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أجريت محاولة تهدف إلى خفض المركبات العضوية المتطايرة أثناء مرحلة نضج مكمورات من المخلفات العضوية المختلفة (مخلفات المدن، مخلفات مصانع السكر، مخلفات بقايا حيوانية، مخلفات بقايا نباتية) عن طريق إضافة ثلاثة أنواع من معادن الطين (المونتموريللنيت، الكاؤولينيت والأتابولجيت) كمعالجة طبيعية. وقد تم تقدير المركبات العضوية المتطايرة من كل من المخلفات العضوية المكمورة تحت الدراسة كملوثات هوائية باستخدام طريقة العضوية المتطايرة تحت أسماء الإيثانول، حامض الخليك، والأسيتون، ، ن-بروبان، سيكلو هكسان، ن-هيبتان، أوكتان، بنزين، كلورو بنزين، إيثيل بنزين، التولوين، داى كلورو ميثان، زيلين، كلوريد الميثيل، وثلاثى كلور إيثان.

توضح النتائج المتحصل عليها إلى أن المركبات العضوية المتطايرة قد سجلت أعلى القيم فى حالة مخلفات مصانع السكر المكمورة، بينما أقلها كانت مصاحبة لمخلفات المدن المكمورة. وعلى الجانب الآخر، أظهرت مخلفات البقايا الحيونية والنباتية المكمورة قيما للملوثات العضوية المتطايرة تمثل مرحلة وسطية بين المخلفات العضوية المكمورة تحت الدراسة. ولذا أمكن ترتيب مكمورات المخلفات العضوية المختلفة تحت الدراسة تبعا لقيم الكميات المنطقة من المركبات العضوية المتطايرة في الترتيب التنازلي التالي: مكمورة مخافات العنات مصانع السكر > مكمورة مخلفات البقايا النباتية > > مكمورة مخلفات البقايا الحيوانية حكمورة مخافات المدن

وحيث أن مخلفات مصانع السكر المكمورة قد أظهرت أعلى القيم من المركبات العضوية المتطايرة، فقد أختيرت للمعالجة الطبيعية باستخدام لمعادن الطين المختبرة (المونتموريللنيت، الكاؤولينيت والأتابولجيت) بمعدلات إضافة ٥، ١٠ ٪ خلال فترتى ٢٤، ٨٨ ساعة. وتوضح النتائج المتحصل عليها أن النسب المئوية للمركبات العضوية المتطايرة كنتيجة لمعالجة مخلفات مصانع السكر المكمورة بمعادن طين المونتموريللنيت، الكاؤولينيت، الأتابولجيت عند معدلات الإضافة ٥ ١٠ ٪ قد وصلت ٢٠ ٢٩ & ٨٧.٥٠ ، ٢٥ % خلال فترتى ٢٤ ، ٢٨ ساعة. وتوضح النتائج السكر المكمورة بمعادن طين المونتموريللنيت، الكاؤولينيت، الأتابولجيت عند معدلات الإضافة ٥ ١٠ ٪ قد وصلت ٢٠ ٢٩ 8 ، ٢٠ ، ٢٠ ٢٦ ٢٢ ، ٢٤ ٢٥ 8 ٢٢ معانة من قيم الكميات المنطلقة فى حالة المكمورات غير المعالجة وذلك بنهاية الوقت المحدد بـ ٢٤ ساعة، مقابل قيم ٩٤ ٩ معادن الطين المختبرة كمعاجة طبيعية تبعا لكفاءتها فى خفض نسب المركبات العضوية المتطايرة عن طريق تقييدها أو الحد من تيسر إنطلاقها فى الترتيب التنازلى المتايرة عن

الأتابولجيت > الكاؤولينيت > المونتموريللنيت.